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THE RADIOLYTIC DECOMPOSITION OF MONOMETHYLHYDRAZINE ROCKET FUEL

by
W. E. Shelberg

U.S. NAVAL RADIOLOGICAL DEFENSE LABORATORY
SAN FRANCISCO • CALIFORNIA • 94135

APPLIED RESEARCH BRANCH
D. L. Love, Head

CHEMICAL TECHNOLOGY DIVISION
R. Cole, Head

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Edward R. Tompkins
Edward R. Tompkins
Associate Scientific Director

D. C. Campbell, CAPT USN
Commanding Officer and Director

ABSTRACT

The storability of monomethylhydrazine (MMH) with respect to solar cosmic, Van Allen belt and nuclear rocket radiations cannot be improved by the addition of free-radical scavengers since the scavengers will fail to suppress the generation of off-gases in MMH by the radiations. This is shown by the inability of normally efficient, olefinic, free-radical scavengers (methyl methacrylate or pentadiene-1,3) to suppress the evolution of off-gas during gamma radiolysis. Accordingly, the radiolytic decomposition of MMH proceeds via a molecular or ionic reaction rather than a diffusion-controlled, free-radical reaction. Gamma radiolysis of a 100-ml specimen to 0.85×10^7 rads produces 227 ml of off-gas (25°C and 1 atm) which is nearly an equimolar mixture of hydrogen (38.7 %), nitrogen (33.5 %), and methane (27.8 %). The average radiation yields (molecules/100 ev) of these gases are 4.7, 4.0 and 3.4, respectively.

The presence of carbon tetrachloride as a free-radical scavenger in MMH increases the nitrogen and methane radiation yields to approximately 30 (a value which is typical of a chain reaction) but does not alter the hydrogen yield significantly. This behavior is attributed to the simultaneous occurrence of two major reactions. One is the aforementioned molecular or ionic reaction that occurs in unadulterated MMH. It produces the expected, nearly equivalent yields of hydrogen, nitrogen and methane. It accounts for all of the hydrogen gas observed in the radiolysis but does not account for all of the nitrogen and methane gases. The other reaction is a chain reaction initiated by the carbon tetrachloride. It produces no hydrogen gas, but produces typically large yields of nitrogen and methane gases. The proposed chain propagating steps are as follows:

$$\cdot CCl_3 + CH_3NHNH_2 \longrightarrow CHCl_3 + N_2 + CH_4 + H\cdot$$

$$H\cdot + CCl_4 \longrightarrow HCl + \cdot CCl_3$$

SUMMARY

Problem

The problem was to determine whether it is possible to suppress the generation of non-condensable gases when monomethylhydrazine (MMH) rocket fuel is subjected to ionizing radiation. The problem is important since gas generated in rocket fuel tanks by solar cosmic, Van Allen, and nuclear rocket radiations might develop excessive pressure and require venting, which is difficult and wasteful of fuel.

Findings

MMH produces more than twice its volume of gas (measured at 25°C and 1 atm.) consisting of hydrogen, nitrogen and methane when irradiated to nearly 10^7 rads with gamma rays. Since it was conceivable that this gas generation proceeds via reactive chemical intermediates known as free-radicals, an attempt at gas suppression was made with chemical additives that could render free-radicals impotent by reacting with them. Two normally efficient olefinic additives (free-radical scavengers) failed to suppress gas evolution, thereby demonstrating that MMH does not decompose radiolytically via free-radical intermediates. Instead, it decomposes via a molecular or ionic process. The addition of carbon tetrachloride as a potential, gas-suppressing additive actually increased gas evolution enormously, and this is explainable on the basis that it initiates a chemical chain reaction.

INTRODUCTION

Large doses of solar cosmic, Van Allen belt, and nuclear rocket radiations will generate copious quantities of non-condensable off-gases in storable liquid rocket fuels. This is indicated by the work of Robinson[1] and Plank[2] who exposed monomethylhydrazine rocket fuel (MMH) to 10^7 rads of gamma radiation and 10^8 rads of reactor radiation, respectively, and noted copious gas evolution. Appreciable gas liberation in a fuel tank at zero gravity in space could result in a non-homogeneous mixture of gas and liquid in various juxtapositions.[3] This might result in uneven combustion and require venting to relieve excessive tank pressure.[3] Venting would be wasteful of liquid fuel and entail undesirable engineering complexities.

A means for suppressing the formation of radiolytic gases would represent an advance in the technology of storable liquid fuels. The possibility of doing this depends upon the mechanism of radiolytic decomposition. Three types of mechanism are possible: molecular, ionic and free-radical. Little can be done if the first two predominate, but should the free-radical process predominate, gas evolution might be suppressed by the addition of a small quantity of a compatible free-radical scavenger. The production of a molecule of non-condensable gas, such as methane, via free-radicals generally involves the radiation-engendered separation of a methyl radical from a solvent molecule, its thermal diffusion, and its abstraction of a hydrogen atom from another solvent molecule. An added free-radical scavenger will react avidly with the methyl radical, breaking the reaction sequence to methane.

The objectives of this study were to investigate the radiolytic decomposition of MMH rocket fuel, and to determine whether it is possible to suppress the generation of radiolytic gases from MMH by the addition of free-radical scavengers. Only experiment could tell whether the free-radical process is important enough in the decomposition of MMH to make the use of free-radical scavengers worthwhile.

The following summary of space and rocket radiations and their dose potentialities to an encased liquid fuel shows that an investigation of space radiation effects in the fuel may reasonably extend over a dose range of 10^6 to 10^8 rads.

The solar cosmic radiation consists essentially of protons. The sun emits large numbers of protons with energies greater than 1 Bev about once every 4.5 years, ordinarily on the descending side of the sunspot cycle. The sun also propagates large numbers of protons with energies between 10 and 500 Mev about once a month for 3 years starting at the maximum of the sunspot cycle. Foelsche[4] has estimated that an interplanetary excursion at about the Earth's distance from the sun from May 1959 to November 1960, a 1.5-year period of high solar proton propagation, could have received a proton dose of approximately 3×10^3 rads behind 1 g/cm^2 of shielding. This amount of shielding is average for a fuel tank.[3] However, much greater proton doses than this might be absorbed should the sun's eruptions become unexpectedly severe and frequent.

The Van Allen belt radiation consists essentially of protons and electrons of substantial energy and flux trapped in two rings by the Earth's magnetic field. The rings surround the Earth in a doughnut fashion and coincide with the geomagnetic equator. The inner ring consists of both protons and electrons, while the outer ring consists almost entirely of electrons. In addition, the nuclear high altitude test on July 9, 1962 injected numerous high energy fission electrons into the inner ring, increasing the dose potentialities to orbiting vehicles significantly. The Van Allen belt radiation is not a serious threat to lunar or planetary vehicles since it can be traversed rapidly or avoided by using a polar trajectory. However, each belt is a significant threat to orbital objects repeatedly exposed to it, each delivering an estimated dose of 10^6 rads/year behind 1 g/cm^2 of shielding.[5] Over 90 percent of this dose is due to bremsstrahlung.

Radiation from nuclear rocket engines is an important problem of the future. Any extensive space program beyond the Apollo missions will be based on nuclear engines. Storable liquid rocket motors on nuclear rockets will be subjected to gamma photons and neutrons, since reactor shielding will be absolutely minimal due to weight limitations. It is reasonable to assume that a storable liquid fuel could receive a dose of 10^8 rads, or more, under these circumstances.

EXPERIMENTAL

The experimental work consisted of preparing degassed specimens of MMH with and without free-radical scavengers, gamma-irradiating them with cobalt-60, and analyzing the non-condensable gaseous products via gas chromatography.

RADIOLYTIC MATERIALS

Monomethylhydrazine

"Anhydrous," rocket-grade MMH produced by the Olin Mathieson Chemical Corporation was used. The fuel was used without additional purification in order to give this study practical value. It contained water and amines, but not more than 2 % by weight. The fuel must be kept under a nitrogen atmosphere to prevent rapid oxidation with the formation of a yellow color. Its container was always flushed with a jet of nitrogen when the cap was removed.

Scavengers

Methyl methacrylate, pentadiene-1,3 and carbon tetrachloride are compatible with MMH and were used as free-radical scavengers. Scavengers such as diphenylpicrylhydrazyl, iodine, benzoquinone and ferric chloride cannot be used. Diphenylpicrylhydrazyl reacts slowly with the fuel to liberate gas, while the others react violently.

The methyl methacrylate was a polymerization grade produced by Rohm and Haas Company. It was inhibited with 60 ppm of hydroquinone.

The pentadiene-1,3 was a 90 percent grade produced by Phillips Petroleum Company, Special Products Division. Its two conjugated double bonds made it a good choice as a scavenger.

The carbon tetrachloride was analytical reagent.

Scavenger Solutions

MMH-scavenger solutions were prepared in a nitrogen atmosphere by pipetting 5 ml of the scavenger into a 100-ml volumetric flask and diluting to volume with MMH.

SPECIMEN PREPARATION

Figure 1 shows an unfilled radiolysis cell sealed to the stopcock (A) of a vacuum manifold. The cell was a 50-ml, pyrex, round-bottom flask fitted with a horizontal break-seal (B), an upward slanted side arm (C), and a seal-off constriction (D). The cell was flushed with nitrogen via the side arm before being filled (A and E open; F closed).

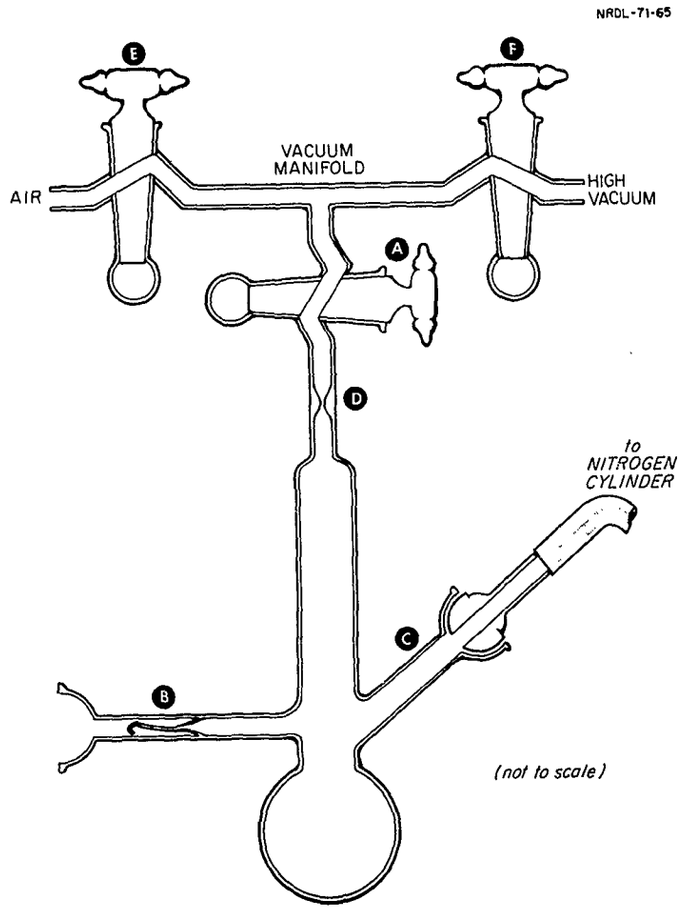

Fig. 1 Unfilled Radiolysis Cell

Some MMH or MMH-scavenger solution was transferred by pipetting from its inconveniently shaped container to a small bottle constantly flushed by a jet of nitrogen. Twenty milliliters were withdrawn from the small bottle with a hypodermic syringe and injected into the cell via the side arm without wetting the side arm. This transfer was performed quickly so that the side arm was disconnected from the nitrogen supply for only a short time.

The specimen was frozen with liquid nitrogen (A closed). The side arm was then warmed with an air-heat gun while the frozen cell was flushed with nitrogen (A and E open; F closed). This served to remove any trace of specimen possibly contaminating the side arm. The side arm of the frozen cell was then sealed off just below its ball joint at atmospheric pressure (A and E open; F closed).

The specimen was then degassed by the conventional vacuum technique of repeated freezing and pumping, and the cell was sealed off at D at 10^{-6} mm Hg.

SPECIMEN IRRADIATION

All specimens were irradiated at 22-25°C to 0.85×10^{7} rads with gamma radiation from cobalt-60. Dosimetry was done with the ferrous sulfate dosimeter which duplicated the specimen in volume and geometry.[6]

PRODUCT ANALYSIS

A 1-liter, gas-storage bulb having two oppositely placed outlets (top and bottom), each consisting of a vacuum stopcock with ball joint, was joined to the top of a Toepler pump. A similar, 10-ml, gas-storage bulb was joined to the top of the liter bulb. This smaller bulb served to aliquot the larger, since the volumes of both bulbs, the volume between the stopcocks that joined them, and the bore volumes of these stopcocks were known from calibration. The Toepler pump system was evacuated to 10^{-3} mm Hg through the top of the smaller bulb.

The irradiated radiolysis cell was joined to the inlet of the Toepler pump via the ball joint of the cell's break-seal. The liquid phase was frozen with liquid nitrogen, and the non-condensable gases

were transferred to the liter storage-bulb and stored at the calibrated volume. An aliquot was then taken with the 10-ml bulb.

The aliquot contained hydrogen, nitrogen and methane which were determined quantitatively by gas chromatography. A Perkin-Elmer gas chromatograph (Model 154), thermistor detector, 50-ft Linde molecular sieve column (30°C), and helium carrier gas were used. The high-vacuum gas-inlet apparatus for gas chromatography previously developed at this laboratory was used.[7]

RESULTS

Table 1 gives product yields for MMH and its scavenger solutions irradiated to 0.85×10^7 rads.

RADIOLYSIS OF MMH, MMH-METHYL METHACRYLATE, AND MMH-PENTADIENE-1,3

Unadulterated, rocket-grade MMH produces a large quantity of radiolytic off-gas. A 100-ml sample generates an average of 227.4 ml of non-condensable gas, measured at 25°C and one atmosphere. The molecular composition is 38.7 % hydrogen, 33.5 % nitrogen, and 27.8 % methane. No detectable oxygen is generated from the small amount of water in the fuel.

The quantity of off-gas is not reduced to any significant extent by the addition of either methyl methacrylate or pentadiene-1,3 as a free-radical scavenger. Thus, the storability of MMH with respect to solar cosmic, Van Allen belt and nuclear rocket radiations cannot be improved by the addition of free-radical scavengers. This result suggests that the off-gas results from a molecular or ionic reaction rather than a diffusion-controlled, free-radical reaction. A mechanism cannot be assigned to the molecular or ionic reaction without further study. This further study would give consideration to the probable uni- or bimolecular nature of the reaction; the nearly equimolecular composition of the off-gas; and the fact that a single molecule of MMH contains the elements of a molecule of hydrogen, nitrogen and methane. Equation 1 is a plausible possibility for the radiolysis, which serves to illustrate these considerations.

TABLE 1

Radiation Yields at 0.85×10^7 Rads

	OFF-GAS (Ml of Gas (25°C and 1 Atm) Generated per 100 ml of Sample)				AVERAGE G (Molecules/100 ev)			
	H_2	N_2	CH_4	Total	H_2	N_2	CH_4	Total
Scavenger: None								
Sample 1	81.4	71.8	58.9	212.1				
Sample 2	99.7	83.0	69.4	252.1				
Sample 3	93.7	74.3	61.6	229.6				
Sample 4	77.4	75.2	63.3	215.9				
Average	88.1	76.1	63.3	227.4	4.7	4.0	3.4	12.1
Scavenger: Methyl Methacrylate								
Sample 1	80.9	85.9	75.7	242.5				
Sample 2	84.5	88.3	78.4	251.2				
Average	82.7	87.1	77.1	246.9	4.4	4.6	4.1	13.1
Scavenger: Pentadiene-1,3								
Sample 1	67.9	67.7	57.9	193.5				
Sample 2	69.3	69.0	58.3	196.6				
Average	68.6	68.4	58.1	195.1	3.6	3.6	3.1	10.3
Scavenger: Carbon Tetrachloride								
Sample 1	62.7	446.0	371.0	879.7				
Sample 2	60.9	699.0	593.1	1353.0				
Average	61.8	572.5	482.1	1116.4	3.3	30.4	25.6	59.3

$$\left[CH_3NHNH_2\right]_n \rightsquigarrow n\ H_2 + n\ N_2 + n\ CH_4 \qquad (1)$$

That the off-gas is not exactly equimolar may be due to molecular or ionic side reactions of a minor nature, or to the inability to achieve better precision in the carefully executed experiments.

There is no a priori reason to believe that the water in the MMH ($\leqslant 2$ %) acts as a free-radical scavenger. Water is actually combined with MMH as CH_3NHNH_3OH, which undergoes basic dissociation to a lesser extent than ammonium hydroxide. Furthermore, Baxendale and Mellows[8] have found that water at a concentration of 3 % in methanol does not scavenge radiolytic free-radicals formed from the methanol. (Uncombined water is structurally and chemically similar to methanol and other simple alcohols, and since these do not self-scavenge their radiolytic free-radicals, one would not expect water to act as a scavenger.[8,9])

RADIOLYSIS OF MMH-CARBON TETRACHLORIDE

The presence of carbon tetrachloride affects the radiolytic decomposition of MMH in a surprising manner. Table 1 shows that the presence of carbon tetrachloride does not affect $G(H_2)$ significantly, but that it increases $G(N_2)$ and $G(CH_4)$ enormously to values typical of chain reactions. The literature reveals that carbon tetrachloride initiates free-radical chain reactions when irradiated in certain solvents.[10,11] The data and the literature together suggest that two major reactions occur simultaneously. One is the expected molecular (or ionic) reaction that occurs in unadulterated MMH. It produces the expected equivalent yields of hydrogen, nitrogen and methane. It accounts for all of the hydrogen gas observed in the radiolysis, but does not account for all of the nitrogen and methane gases. The other reaction is a chain reaction initiated by the carbon tetrachloride. It produces no hydrogen gas, but does produce yields of nitrogen and methane that are typical of chain reactions.

Concerning the proposed chain reaction, radiolysis of the carbon tetrachloride is a prerequisite. This proceeds via Eq. 2 according to Chen and to others.[12,13]

$$CCl_4 \rightsquigarrow Cl\cdot + \cdot CCl_3 \qquad (2)$$

Either of the reactive radicals from carbon tetrachloride will abstract a hydrogen atom from a suitable solvent and generate a new radical to propagate a chain.[10,12,14] Equations 3 and 4 provide an example from Hannerz's work.[10]

$$\cdot CCl_3 + R_1R_2CHOH \longrightarrow CHCl_3 + R_1R_2\dot{C}OH \qquad (3)$$

$$R_1R_2\dot{C}OH + CCl_4 \longrightarrow HCl + R_1R_2CO + \cdot CCl_3 \qquad (4)$$

For the case where the solvent is MMH, Reactions 5 and 6 are proposed, taking into account (1) the hydrogen abstraction, (2) the probability of a bimolecular reaction, (3) the requirement of producing nitrogen and methane gases in equivalent amounts, (4) the requirement of not producing hydrogen gas, and (5) the necessity of generating a new radical for chain propagation.

$$\cdot Cl + CH_3NHNH_2 \longrightarrow HCl + N_2 + CH_4 + H\cdot \qquad (5)$$

$$\cdot CCl_3 + CH_3NHNH_2 \longrightarrow CHCl_3 + N_2 + CH_4 + H\cdot \qquad (6)$$

$$H\cdot + CCl_4 \longrightarrow HCl + \cdot CCl_3 \qquad (7)$$

Reactions 5 and 6 produce two hydrogen radicals between them, and these propagate two identical chains. In the next chain step, a hydrogen radical is scavenged by the carbon tetrachloride according to Reaction 7. Thus, the chain reaction in MMH would consist of the alternate occurrence of Reactions 6 and 7.

The matter of relative reactivity of carbon tetrachloride and MMH with hydrogen radicals is important. One must conclude that the carbon tetrachloride completely scavenges hydrogen radicals produced via Reactions 5 and 6, in spite of the high chemical reactivity of MMH. If this were not true, the hydrogen radicals would almost certainly abstract with MMH molecules to produce hydrogen gas, and the value for $G(H_2)$ would be much greater than the observed value of 3.3, which is wholly accounted for by the molecular or ionic reaction. Reaction 7 occurs readily, being one of the steps in the commercial manufacture of chloroform.

Approximately 210 molecules each of nitrogen and methane are produced before a chain is terminated. This may be calculated from the G values for MMH-carbon tetrachloride radiolysis in Table 1, a value of 2.6 for $G(\cdot Cl) + G(\cdot CCl_3)$ for pure carbon tetrachloride,[12] and an estimation that the carbon tetrachloride (5 percent by volume) absorbs 5 % of the total energy input. Perhaps chain termination occurs because the propagating free-radicals combine, although other, indeterminate reactions may be responsible. The irradiated MMH-carbon tetrachloride solutions contain about ten-fold the amount of carbon tetrachloride required to produce the quantity of nitrogen and methane attributed to the chain reaction, that is, the quantity of nitrogen or methane found to be in excess of that expected from the molecular or ionic reaction.

As a last point of interest, the apparent ability of carbon tetrachloride to scavenge hydrogen radicals successfully in MMH increases one's confidence that methyl methacrylate and pentadiene-1,3 would have scavenged free-radicals successfully in MMH-methyl methacrylate and MMH-pentadiene-1,3 had MMH generated primary, radiolytic free-radicals. While these olefins can undergo radiolysis in MMH solution to produce hydrogen and other free radicals, they act as self-scavengers and cannot, therefore, initiate a chain reaction leading to hydrogen, nitrogen or methane gas.

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gases. The other reaction is a chain reaction initiated by the carbon tetrachloride. It produces no hydrogen gas, but produces typically large yields of nitrogen and methane gases. The proposed chain propagating steps are as follows:

$$\cdot CCl_3 + CH_3NHNH_2 \longrightarrow CHCl_3 + N_2 + CH_4 + H\cdot$$

$$H\cdot + CCl_4 \longrightarrow HCl + \cdot CCl_3$$

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